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INFLUENCE OF CELLULOSE ETHER PARTICLE SIZE ON WATER RETENTION OF FRESHLY-MIXED MORTARS

By

L. Patural ¹, A. Govin ¹, P. Grosseau ¹, B. Ruot ², O. Devès ³

¹ École Nationale Supérieure des Mines de Saint-Étienne,

Centre SPIN, LPMG UMR 5148

158 Cours Fauriel, F-42023 Saint-Étienne Cedex 2, FRANCE

Tel : +33 (0)4 77 49 97 77

Fax : +33 (0)4 77 49 96 94

E-mail: patural@emse.fr

² Centre Scientifique et Technique du Bâtiment (CSTB)

Département Enveloppe et Revêtements / Division Caractérisation Physique des Matériaux

24 Rue Joseph Fourier, F-38400 Saint-Martin-d'Hères, FRANCE

³ Centre Scientifique et Technique du Bâtiment (CSTB)

Département Enveloppe et Revêtement / Division Enduits, Mortiers et Colles

84 Avenue Jean Jaurès - Champs-sur-Marne

F-77447 Marne-la-Vallée Cedex 2, FRANCE

Influence of cellulose ether particle size on water retention of freshly-mixed mortars

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ABSTRACT

Cellulose ethers are polymers frequently introduced into mortar formulations in order to improve water retention capacity and workability of the freshly mixed materials. Cellulose derivatives can induce excellent water retention thanks to the possible superposition of two phenomena. Mortar rheology can impact water retention, increasing media viscosity. Other specific effects provided by cellulose ethers may improve water retention, though this effect remains misunderstood until now. These admixtures may act as a diffusion barrier, preventing water loss, or they can modify the porous network in the fresh state. Physico-chemical parameters of the admixtures (molecular weight, granulometry, etc) seem to have a strong influence on mortar water retention capacity.

Keywords: cellulose ethers, mortar, particle size, water retention.

INTRODUCTION

Factory-made mortars are mainly composed of mineral binders (cement, lime and/or gypsum), aggregates and additives (e.g. fillers). They also contain different kinds of admixtures, mostly organics (such as latexes and polysaccharides), in order to impart some specific properties to the mortar, from the fresh paste to the hardened material [1]. Among all the polysaccharides, cellulose ethers seem to be the most suitable molecules to produce mortars with adequate water retention ability (i.e. higher than 94% up to 99%).

Mortar consistency may contribute to its water retention capacity, but this hypothesis should be checked by further investigations. Indeed, cellulose ethers can induce excellent water retention thanks to the possible superposition of two phenomena [2]:

- a rheological effect similar to the one produced by other polysaccharides
- an effect that could be specific to cellulose ethers, which remains to be defined.

Possibilities include modification of the porous network in the fresh state, osmotic pressure, or the presence of a cellulose ether film acting as a diffusion barrier [3].

Using well-known molecules, it should be possible to understand the function of three types of cellulose ethers on mortar water retention. Particle size and morphology of cellulose ether powders are two parameters which are expected to influence mortar water retention. Here, the influence of cellulose ether particle size on water retention has been studied to understand if both parameters are linked.

MATERIALS AND METHODS

Mineral products

Mortars were prepared with “CEReM formulation”. A dry mixture was prepared with 30% cement, 65% normalised sand and 5% filler. Grey Portland cement was CEM I 52.5 N according to EN 197-1 [4]. Chemical analysis was performed by X-ray fluorescence spectroscopy (XRF). Then, phase compositions (Table 1) were calculated using Bogue formula with CaO correction [5].

Table 1. Chemical and phase composition of the investigated cement.

Chemical composition (% wt)				Phase composition (% wt)	
<i>Oxides</i>	<i>XRF</i>	<i>Oxides</i>	<i>XRF</i>	<i>Phases</i>	<i>XRF (Bogue)</i>
CaO	66.3 ± 0.2	MgO	0.99 ± 0.01	C ₃ S	64.3 ± 0.8
SiO ₂	22.3 ± 0.1	P ₂ O ₅	0.24 ± 0.01	C ₂ S	15.5 ± 0.3
Al ₂ O ₃	3.40 ± 0.01	TiO ₂	0.18 ± 0.18	C ₃ A	4.2 ± 0.1
SO ₃	3.04 ± 0.03	K ₂ O	0.04 ± 0.04	C ₄ AF	8.7 ± 0.1
Fe ₂ O ₃	2.87 ± 0.03	MnO	0.016 ± 0.001	Sulphates	3.04 ± 0.03

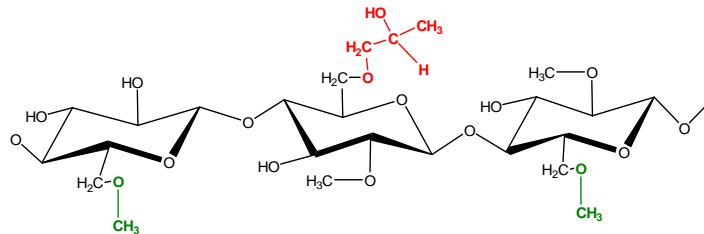
Each experiment was performed three times with the results averaged for the three measurements. The filler reference was CaCO₃. The organic admixture amount (0.27%) was based on the total dry mixture (i.e. cement, sand and filler). The W/C was 1. Mixing procedure was in accordance with EN 196-1 [6].

Organic admixtures: cellulose ethers

Admixtures are especially formulated products, added in small amounts to mortar during the mixing process in order to improve its properties.

Cellulose, the most abundant polymer in nature, forms a part of the polysaccharide family and is derived from β -D-glucopyranose. Cellulose ethers are obtained by alkalization or alkylation of cellulose. In this work, three kinds of cellulose ethers were studied: **hydroxypropylmethyl cellulose**, noted HPMC (Fig. 1a), **hydroxyethylmethyl cellulose**, noted HEMC (Fig. 1b) and **hydroxyethyl cellulose**, noted HEC (Fig. 1c).

(a)



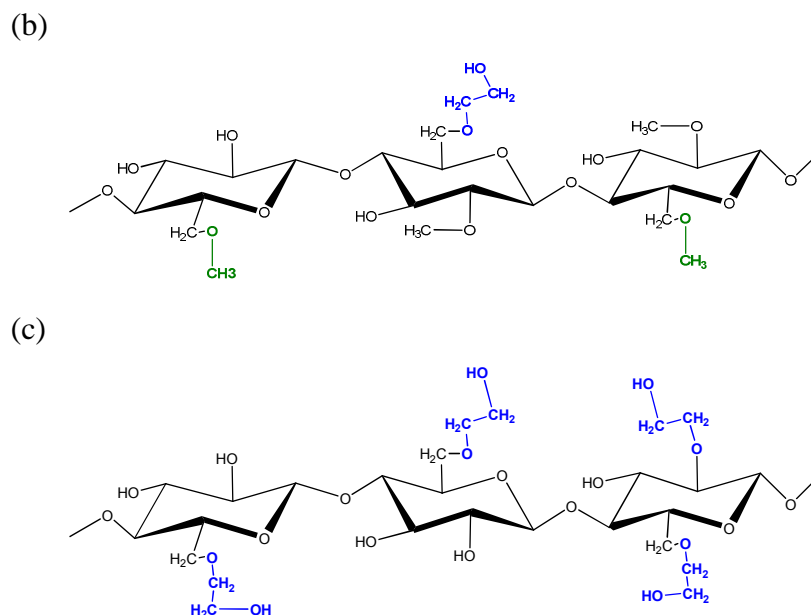


Fig. 1. Molecular structure of cellulose ethers ((a) HPMC, (b) HEMC, (c) HEC).

On Figs. 1a, 1b, and 1c, substituent positions are arbitrary; they differ from one molecule to another. Ten cellulose ethers were selected to study particle size influence on water retention: 4 HEC, 3 HEMC and 3 HPMC (Table 2). These cellulose derivatives are widely used in many industrial fields of application such as cosmetics, pharmaceuticals, paints, textiles and mineral industries. In building materials, cellulose products are used as water-retaining agents, thickeners, binders, and film formers.

Table 2. Cellulose ethers (HEC – HEMC – HPMC) used in this work.

HEMC	\overline{M}_w (kDa)	Hydroxyethyl group (% OC ₂ H ₄ OH)	MS	Methoxy group (% OCH ₃)	DS
C2	180	4.8	0.15	27.4	1.7
C4	380	4.8	0.15	27.4	1.7
C7	660	9.0	0.29	23.8	1.5
HPMC	\overline{M}_w (kDa)	Hydroxypropyl group (% OC ₃ H ₆ OH)	MS	Methoxy group (% OCH ₃)	DS
J1	225	2.98	0.1	28.2	1.75
J2	630	2.98	0.1	28.2	1.75
J3	910	2.98	0.1	28.2	1.75

HEC	\overline{M}_w (kDa)	Hydroxyethyl group (% OC ₂ H ₄ OH)	MS
H1	45	45.3	1.9
N1	40	56.0	2.5
H7	790	52.5	2.4
N4	1 500	56.0	2.5

The number of substituted hydroxyl groups (OH) per anhydroglucose unit is expressed as DS (Degree of Substitution). Moreover, the molar ratio of alkoxy groups (hydroxypropyl, hydroxyethyl, and methoxy) in the side chains to cellulose is expressed as the average Molecular Substitution (MS).

All polysaccharides were analysed by Size Exclusion Chromatography (SEC) in order to determine their average molecular weights [7]. This chromatographic method separates molecules relating to their size. SEC analysis was performed on a Waters apparatus equipped with a pump (Waters 916) and a refractometer-type detector (Waters 2410). The specific column used for polysaccharide SEC was a Tosohaas TSK Gel GMPWXL column. The eluent was a 0.5 mol/L sodium chloride solution in order to avoid agglomeration. It was filtered and in line-degassed. The flow rate was set to 0.5 mL/min. The column was kept at 35°C in an oven.

Cellulose ethers particles size separation

To separate cellulose ethers powders, a sieve shaker was used in order to divide the powders into 4 or 5 fractions ranging from 100 to 200 μm .

The particle size distribution was then measured using a laser diffraction granulometer (Mastersizer 2000, Malvern), in dry dispersion.

Cellulose ethers dissolution rate

The cellulose ether dissolution rate was monitored in saturated lime solution in order to be close to CEReM mortar conditions (high pH value). The admixture quantity was adjusted to obtain a polysaccharide concentration of 9 g/l (equivalent to CEReM mortar). Experiments were performed in a glass reactor controlling the temperature at 23°C. The stirring system consisted of a turbine with four blades.

The cellulose ether concentration was determined using a colorimetric method described by Dubois [8]. This method consists of adding 0.25 mL of 80% phenol solution and 1.3 mL of sulphuric acid to 0.5 mL of supernatant (obtained after 5 minutes centrifugation) in tubes, which were then closed and vortex-stirred. After cooling down for 20 minutes, the solution absorbance was measured at 490 nm using a UV/Visible spectrophotometer (CARY 300 Scan, Varian).

Water retention measurements

Water retention is a mortar property that prevents the rapid loss of water to substrate by suction (and also water to air, to a lesser extent). This property prevents bleeding or “water loss” when the mortar is in contact with relatively permeable units. It is a fundamental property, which affects workability and bond between mortar and masonry units. The degree of water retention will depend on the mortar formulation.

According to the DTU 26.1 [9], mortars are divided into three classes. The first one is for mortars which have water retention lower than 86%; they belong to the low water retention category. The second class (intermediate water retention) corresponds to values ranging from 86% to 94%. The last one, defined by water retention higher than 94%, corresponding to the required values, is related to strong water retention mortars. These limits have to be handled with care as they refer to ASTM C91 measurements [10]. In this study, water retention measurements were performed using two different standardized methods: standard DIN 18555-7 [11] and standard ASTM C91. Our results showed that both methods produce similar results (see “Correlation between ASTM C91 and DIN 18 555-7 test methods”). Consequently, only ASTM measurements will be presented in this paper.

ASTM measurements have to be performed 15 minutes after mixing. The aim of the test is to measure the water loss of a mortar under a 50 mm Hg (6.6×10^3 Pa) vacuum for 15 minutes (Fig. 2).

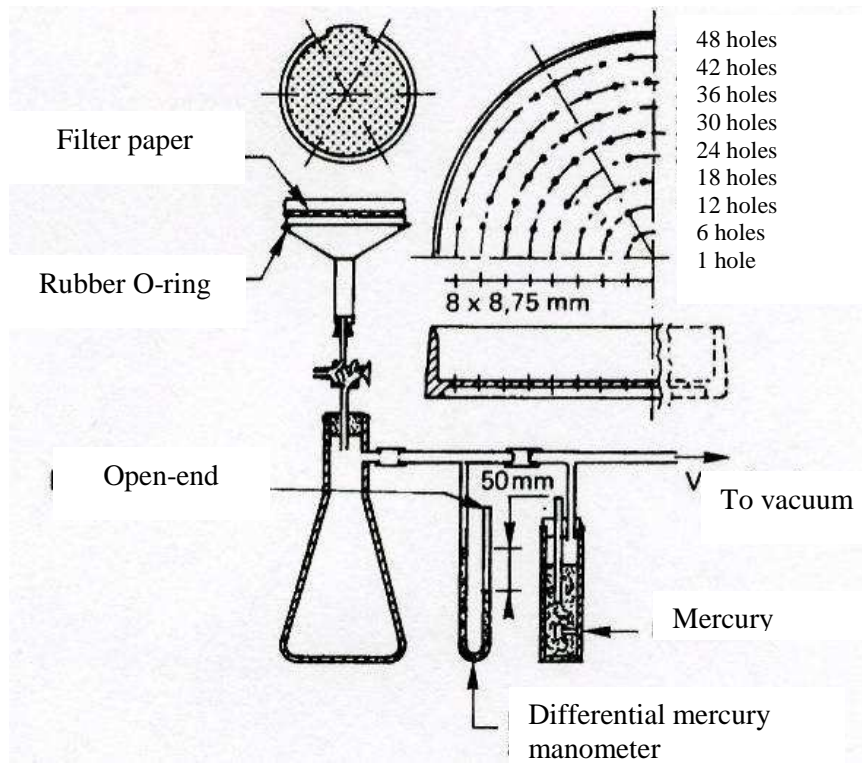


Fig. 2. Experimental device to measure water retention with standard ASTM C91.

Then, the water retention capacity, noted as WR , is calculated using the following equation:

$$WR \ (%) = \frac{W_0 - W_1}{W_0} \times 100$$

W_0 represents the initial mass of mixing water, and W_1 is the mass of mixing water lost after 15 minutes under depression.

Results and Discussion

Correlation between ASTM C91 and DIN 18 555-7 test methods

The comparison between both methods is shown on Fig. 3. Usually, both methods produce relatively comparable results, except for the three HEC samples, which imparted a more fluid property to the mortar. The water retention value obtained with the DIN method was close to 90% while the result of ASTM was higher (roughly 97%). This could be explained by a bleeding phenomenon observed for these admixtures during the experiment.

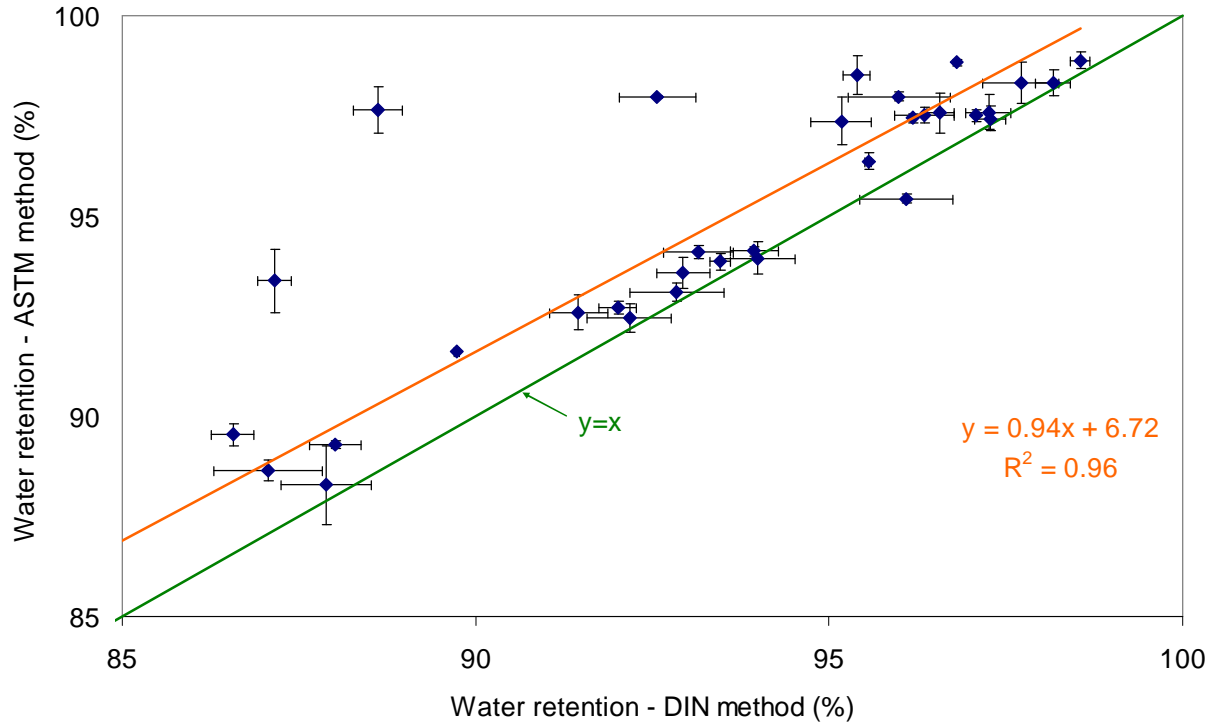


Fig. 3. Comparison between the DIN and the ASTM method.

Overall, the ASTM values were generally slightly higher than those obtained with the DIN method. This phenomenon could be explained by a depression effect. Indeed, the ASTM measurement was carried out with a depression of 50 mm Hg, while the DIN method measured mortar water absorption in contact with a filter paper, based on gravity and capillarity, and performed at atmospheric pressure.

All things considered, the DIN 18555-7 and the ASTM C91 methods are two ways of water retention determination, which are roughly comparable.

Cellulose ethers: effect of particle size

First, granulometry results were generally slightly higher than the cut threshold results of the sieve. This could be explained by cellulose ether particle shape. Indeed, some of the particles have a fibre like appearance.

HEC

Cellulose ether particle size is generally considered as a key parameter influencing mortar water retention. First, the effect of HEC particle size was investigated. Among the four HEC samples, the main difference was the molecular weight. H1 and N1 had low molecular weights (respectively 45 and 40 kDa), whereas H7 and N4 had higher molecular weights. On

the one hand, H1 and N1 particle size had an effect on mortar water retention (Fig. 4). Indeed, for H1, water retention capacity ranged from 87% to 94% for particle sizes ranging from 150-200 μm to a diameter lower than 100 μm , respectively. Thus, for low molecular weight HEC, the smaller the particles, the better the water retention. Moreover, H1 and N1 had equivalent molecular weight whereas MS increased from 1.9 to 2.5, respectively. Water retention was equal to 95% for H1, and equal to 93% for N1. Thus, for constant molecular weight HEC, water retention decreased when MS increased.

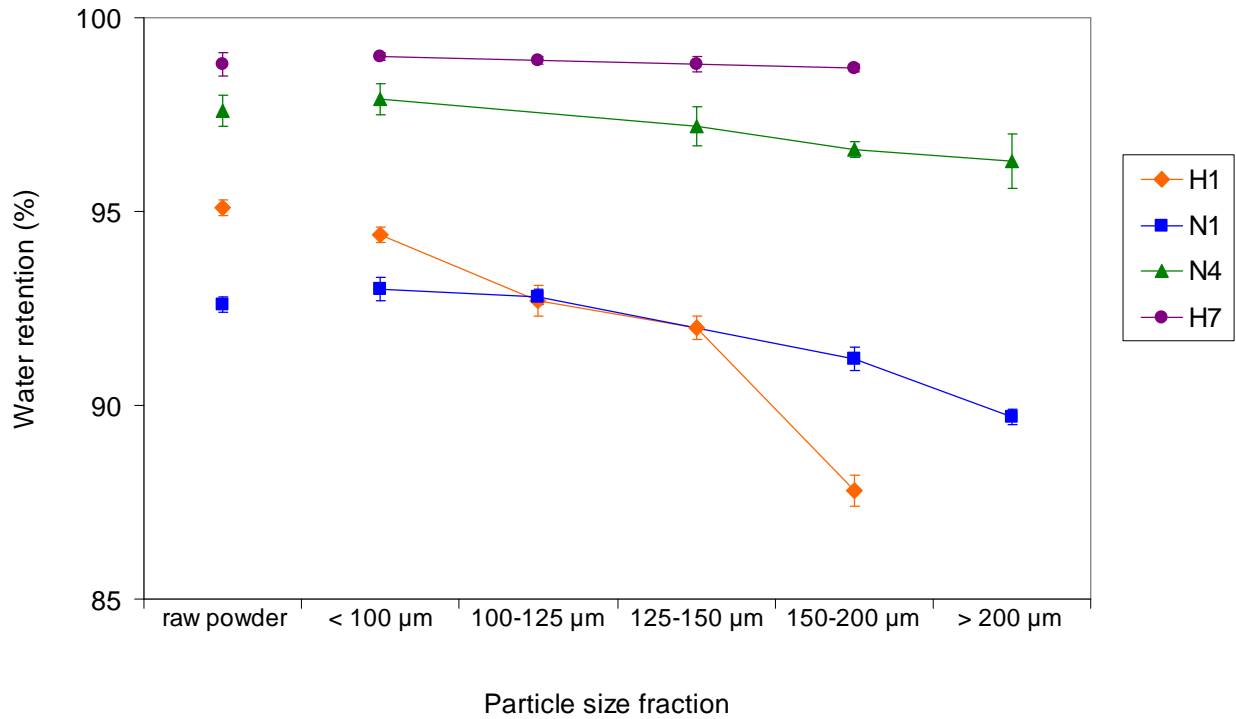


Fig. 4. Influence of HEC particle size on water retention.

On the other hand, for N4 (1 500 kDa), particle size impact was weaker than with the H1 and N1. Actually, for the thinner fraction (diameter lower than 100 μm), water retention was equal to 98%, whereas, for the thicker fraction (diameter higher than 200 μm), water retention capacity was about 96%. Afterwards, for H7 (790 kDa), the water retention was similar, and was roughly equal to 99% independent of the particle size. As for low molecular weight HEC, MS seemed to influence water retention. While molecular weight increased from 790 kDa (H7) to 1 500kDa (N4), MS slightly increased from 2.4 to 2.5, and water retention decreased from 99% to 98%.

To summarize the influence of particle size for HEC, HEC with low molecular weights, the thinner the particles, the better the water retention. On the contrary, for HEC with high

molecular weights, the influence is weak or not relevant. MS impact was noticed for both HEC groups: water retention decreased when MS increased.

HEMC

Among this group, molecular weight increased between C2 to C4. C7 had a higher molecular weight and a higher MS than C2 and C4. First, for HEMC C2 (Fig. 5), mortar water retention varied for every particle size fractions. No real trend is evident. Fractions #3 (125-150 μm) and #1 (<100 μm) had the lowest water retention values (about 93%). Two others fractions, #4 (150-200 μm) and #2 (100-125 μm), provided higher water retention capacities. These differences may be explained by differences in morphology, or molecular weight. For HEMC C4, mortar water retention was roughly constant and independent of the particle size. Finally for C7, despite an increase in molecular weight, water retention was lower than C4. This could be explained by an increase in MS from 0.15 to 0.29 from C4 to C7.

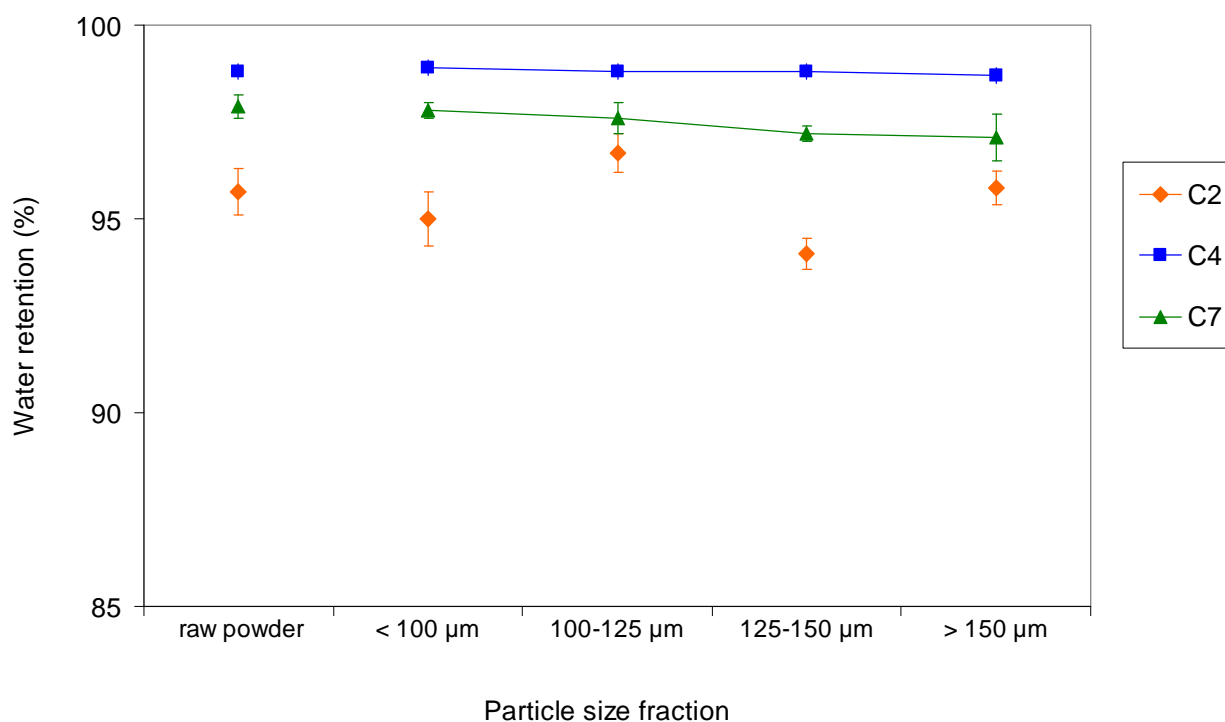


Fig. 5. Influence of HEMC particle size on water retention.

HPMC

HPMC group was composed of three polymers with the same substitution degrees (DS = 1.75 and MS = 0.1), while molecular weight increased from J1 to J3.

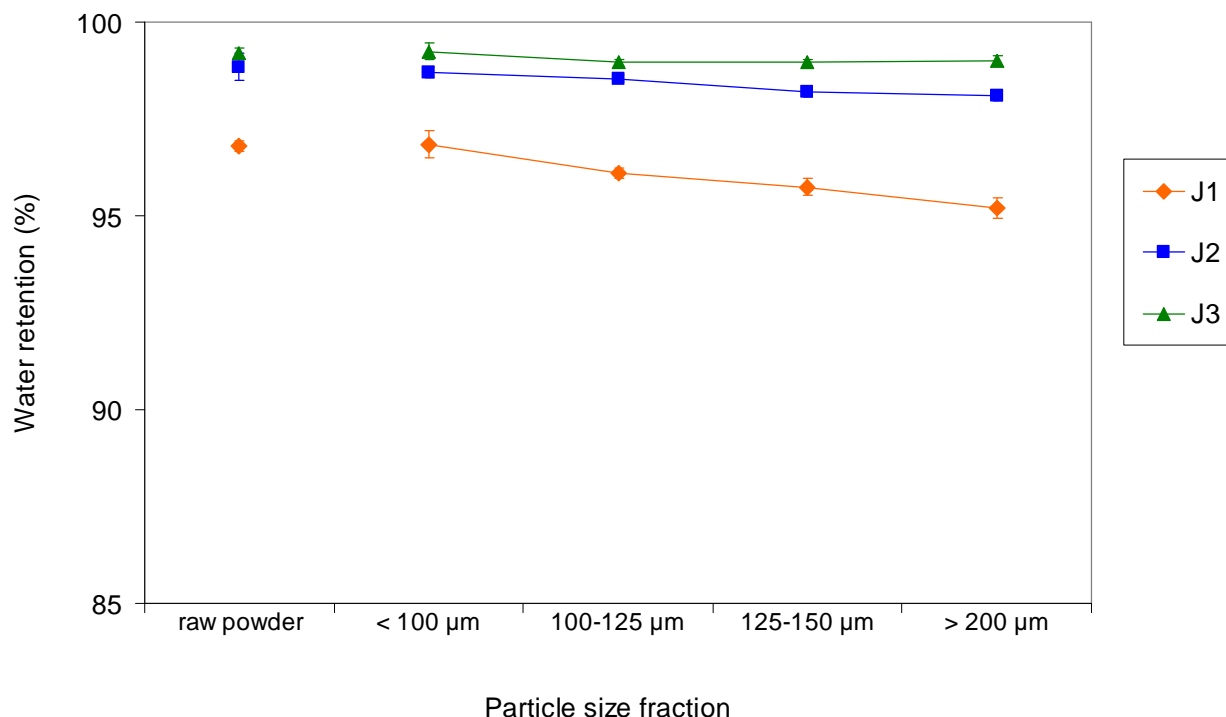


Fig. 6. Influence of HPMC particle size on water retention.

J1 particle size influenced water retention capacity (Fig. 6). As a matter of fact, water retention increased while particle size decreased. However, for J2, this influence was weaker. Water retention ranged from 98% to 99% while particle size ranged from 150-200 µm to less than 100 µm. Finally, J3 did not influence mortar water retention.

In conclusion, two different behaviours were highlighted. Particle size influenced water retention for cellulose ethers with low molecular weights, whereas, for higher molecular weights cellulose ethers, particle size influence was smaller or not significant.

To explain these two behaviours, two hypotheses can be proposed. For the first one, particle size influence may be explained by a difference in dissolution rate for each particle size fraction. For the second class, it could be interpreted by the presence of a cellulose ether concentration threshold value. Indeed, from this threshold, mortar water retention was still constant and independent of the cellulose ether concentration.

Cellulose ether dissolution rate

As observed for HEC H1, the thinner the particles, the better the water retention. The dissolution rate of every particle size fractions was performed for this admixture.

Dissolution rate was monitored for the thinnest ($< 100 \mu\text{m}$) and the thickest fraction ($150\text{--}200 \mu\text{m}$) of H1 (Fig. 7). As expected, the thinnest fraction dissolved faster than the thickest fraction. Indeed, to dissolve 90% of the total cellulose ether quantity, 11 minutes were needed for the fraction lower than $100 \mu\text{m}$, whereas 24 minutes were required for the fraction ranging from 150 to $200 \mu\text{m}$.

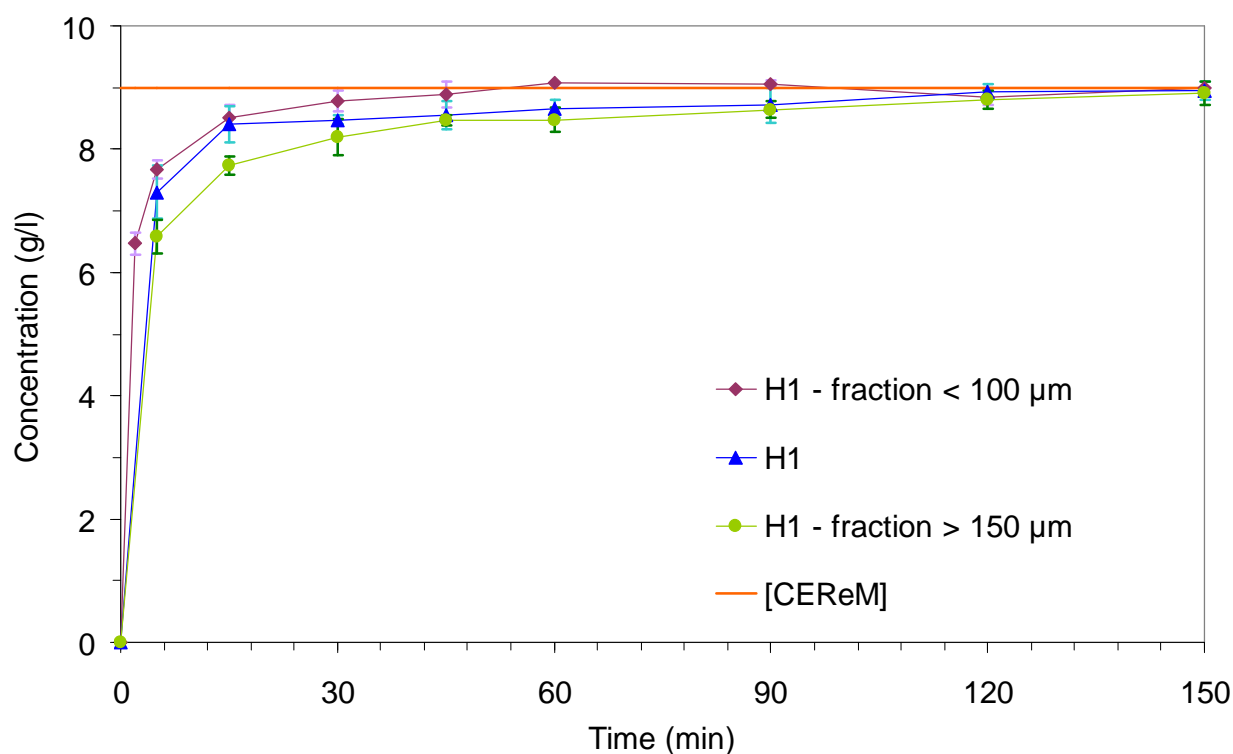


Fig. 7. Dissolution rate of H1 and its particle size fractions.

In conclusion, a particle size decrease corresponds to an increase in dissolution rate of these particles and, consequently, in mortar water retention. For the thinnest particles, the water retention values were higher because the suitable soluble cellulose ether quantity was reached in less time. On the contrary, for thicker particles, when water retention measurements were performed, the particles were not totally dissolved.

Influence of cellulose ether concentration

When particle size has no effect on mortar water retention, there may exist a threshold value in admixture concentration above which water retention remains constant. To check this hypothesis, the water retention was studied as a function of the cellulose ether concentration. In Fig. 8, the water retentions of two HEC samples are shown.

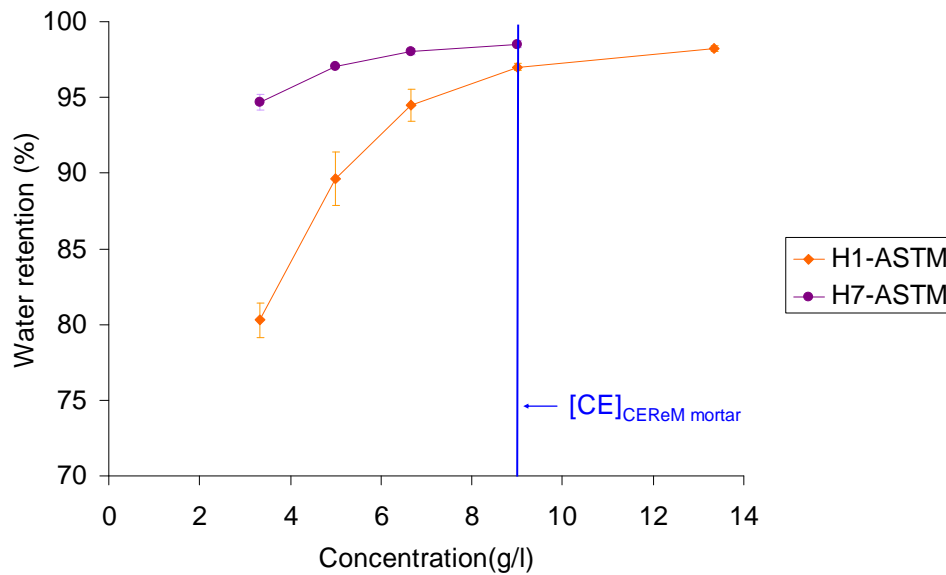


Fig. 8. Influence of HEC concentration on water retention.

First, when H1 concentration increased from 3.3 g/L to 13.3 g/L, the water retention increased from 80% to 98%. However, for HEC H7, the water retention corresponding to a cellulose ether concentration of 9 g/L (CEReM mortar conditions) seemed to be reached at a lower concentration (roughly $[H7] \approx 5-7$ g/L). Consequently, whatever the particle size, if the solution contains an adequate amount of solubilised polymer, the water retention will not change.

Conclusion

Addition of cellulose ether increases mortar water retention. This property was influenced by polymer particle size depending on admixture molecular weight. Indeed, for low molecular weight cellulose ethers (providing an intermediate water retention), the thinner the particles, the stronger the water retention capacity. This behaviour was explained by differences in dissolution rate of each particle size fraction. On the contrary, for high molecular weight

cellulose ethers (providing a strong water retention), the impact of particle size was very small or not significant. In fact, water retention was not affected by this parameter because the suitable polymer quantity could be reached independent of the particle size fraction. Then, water retention does not change. However, these results should be handled with care. For high molecular weight polymer, as the water retention was very high, the influence of particle size may not be observed because water retention values could be too high. Besides, the methods used in this study could not sufficiently discriminate water retention differences with such cellulose ethers.

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